METHANE/STEAM REFORMING

Methane and steam react chemically at elevated temperatures, and the reaction is accelerated by the presence of a nickel catalyst. The products produced from the chemical reaction are a mixture of carbon oxides, hydrogen, water vapor and unreacted methane. Two reversible chemical reactions are occuring, the exothermic shift reaction, and the endothermic reforming reaction. The second law of thermodynamics sets the free energy and the resulting equilibrium chemical composition of the gas mixture. Catalyst produce essentially equilibrium conditions in a commercial reactor. Three variables set the equilibrium conditions; temperature, pressure, and the steam-to-methane ratio. By way of example, the two parallel reactions, heats of reactions, $\triangle H$, and the equilibrium constant, K at 1000°F are:

1) Reform $CH_4 + H_2O \xrightarrow{1000F} CO + 3H_2$ $\triangle H_R = 95{,}880$ Btu/mole, $K_R = .049$

2) Shift $CO + H_2O \xrightarrow{1000F} CO_2 + H_2$ $\triangle H_S = -15{,}878$ Btu/mole, $K_S = 3.479$

Chemical reactions at equilibrium compel precise ratios, K, of reactants and products. If the pressure of the methane/steam mix is assumed to be 500 psia and the steam-to-methane ratio,N, is assumed to be 5/1, values of X and Y are calculated as follows:

Let X = number of moles of methane reacting
and Y = number of moles of CO reacting
N = steam-to-methane ratio
P = total pressure in atmospheres

Reform: $\dfrac{(X-Y)(3X+Y)}{(1-X)(N-X-Y)(N+1+2X)^2} = \dfrac{K_R}{P^2}$ Shift: $\dfrac{Y(3X+Y)}{(X-Y)(N-X-Y)} = K_S$

Solving both equations simultaneously: X = .215547 & Y = .205357
The chemical composition of the equilibrium mixture (both wet and dry basis) and net heat of reaction for this example can be calculated, as follows:

Component	Mole % (wet)	Mole % (dry)
Methane	12.198	42.358
Hydrogen	13.348	46.005
Carbon monoxide	.158	.548
Carbon dioxide	3.193	11.089
Water vapor	71.203	0.000
Total	100.000	100.000

Energy required for chemical reaction: X(95,880) + Y(-15,878) = 17,425 Btu/mole
Partial pressure of steam in feed mixture is 5/6(500) or 417 psia: 448°F dew pt.
Energy to heat mixture from dew pt. to 1000°F: = 5(4876) + 7333 = 31,713 Btu/mole
Thus, the total heat required in the reforming zone = 49,138 Btu/mole
Chemical energy is seen to be 17,425/49,138, or 35.46% of that required.